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ENCAPSULATED ENZYME PREPARATION WITH IMPROVED SOLUBILITY

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Abstract

An encapsulation system was to be developed for dust-free enzyme granulates which, by uniform application onto an enzyme containing granulate, counteracts the surficial destruction of the granulate, increases the storage stability of the enzyme by a protective encapsulation of the entire granulate, permits masking of intrinsic coloration of the unencapsulated enzyme granulate, possibly removes the offensive odor of the unencapsulated granulate, and assures the solubility of the encapsulated granulate. This was substantially attained by making available an enzyme granulate containing enzyme and inorganic and/or organic carrier material and a uniform pigment containing encapsulating layer of an encapsulating system that contains 5-70 wt% finely particulate inorganic water-insoluble pigment, 45-90 wt% water-soluble organic material that is solid at room temperature with a melting point in the range of 45-65°C, and up to 20 wt% pourability improving agent.

Description

The present invention pertains to an enzyme granulate, a process for its preparation, and use of the granulate in powdered detergents and cleaning agents.

Enzymes, especially proteases, find a large application in detergents, detergent aids, and cleaning agents. The enzymes are usually not used as concentrates but as mixtures with diluting and carrier materials. If such enzyme preparations are mixed into conventional detergents, there can be substantial degradation of the enzyme activity during storage, especially if bleaching

compounds are present. Application of the enzyme to carrier salts with concurrent granulation, as per German Patent No. 16 17 190 Offenlegungsschrift or by adhesion to nonionic surfactants as per German Patent No. 16 17 188 Offenlegungsschrift does not lead to notable improvement in the storage stability since the sensitive enzymes in such mixtures are generally found on the surface of the carrier substance. Although the storage stability of the enzymes can be substantially increased, if the enzymes are enclosed by the carrier material or are embedded therein and are subsequently converted into the desired particulate form by extruding, pressing, and Marumerizing into the desired particulate form such as in, for example, German Patent No. 16 17 232, German Patent No. 20 32 768 Offenlegungsschrift, and German Patent Nos. 21 37 042 and 21 37 043 Auslegungsschriften. However, such enzyme preparations have inadequate dissolving properties. The undissolved particles can become entrained in laundered goods and contaminate it, or they are transferred to the wastewater without being used. Although embedding agents known from German Patent No. 18 03 099 Offenlegungsschrift consisting of a mixture of solid acids or acid salts, carbonates or bicarbonates dissolve upon addition of water which improves the dissolving capability, they are, in turn, very sensitive to moisture and thus require additional protective measures.

From European Patent No. 168 526, enzyme granulates are known that contain starch, zeolite, and water-soluble granulating aids swelling in water. In that document, a preparation process is proposed for such formulations which consists essentially of concentrating a fermenter solution that has been freed of insoluble components, mixing it with the additives, granulating

the mixture obtained, and possibly coating the granulate with film forming polymers and dyes. The process with the additive mixture proposed there is advantageously done with fermentation solutions that have been concentrated to a relatively high solids content, for example 55 wt%. However, the granulates prepared in this manner have such a high dissolution or decomposition rate under washing conditions that the granulate is already partly decomposed relatively quickly during storage and the enzymes are deactivated.

From International Patent Application No. 92/11347, enzyme granulates for use in powdered detergents and cleaning agents contain 2-20 wt% enzyme, 10-50 wt% starch with swelling capacity, 5-50 wt% water-soluble organic polymers as granulating aid, 10-35 wt% cereal flour, and 3-12 wt% water. Due to such additives, processing of the enzyme is possible without substantial activity losses.

From International Patent Application No. 93/07263, an enzyme containing granulate consists of a water solubility or dispersible core which is coated with a vinyl polymer on which there is a layer of enzyme and vinyl polymer, wherein the granulate has an outer coating of vinyl polymer. The outer coating can also contain pigments. However, due to the multilayer structure, such an enzyme granulate is relatively expensive to produce.

From International Patent Application No. 95/02031, encapsulated enzyme granulates are known whose encapsulating coating consists of an encapsulating system containing 30-50 wt% finely particulate inorganic pigments, 45-60 wt% of an alcohol that is solid at room temperature with a melting point in the range of 45-65°C, up to 15 wt% emulsifier for the alcohol, up to

5 wt% dispersant for the pigment, and up to 3 wt% water. Due to the presence of relatively large amounts of water-insoluble fatty alcohols, such enzyme granulates during dissolution in water can lead to residue problems since the presence of the emulsifier is often inadequate to dissolve the organic parts of the encapsulation system.

From International Patent Application No.93/07260, a preparation process is disclosed for a dust-free enzyme granulate, which comprises spray application of a fermentation broth onto a hydrated carrier substance, and a subsequent spray application of a solution with certain encapsulating materials including fatty acid esters, alkoxylated alcohols, propylvinyl alcohol, polyethylene glycol, sugar, and starch, and evaporation of the solvent.

The encapsulating mass used in the documents indicated for the outer encapsulating layer are normally applied to the enzyme granulate in the form of an aqueous dispersion in a fluidized bed dryer. In this, there is the danger of at least surface destruction of the granulate by dust abrasion in the fluidized bed that can lead to an increased proportion of extremely finely particulate material in the enzyme granulate which is not usable in conventional powdered detergents or cleaning agents since it does not distribute itself homogeneously in the resulting mixture, and moreover, enzyme-containing fine dust can lead to allergic reactions by the user of the detergents. For this reason, one strives to maintain the proportion of fine particles in the enzyme granulate as low as possible so as to have to remove as little as possible by screening or air separation. Moreover, the use of encapsulating materials in dissolved form is

disadvantageous since the solvent applied to the enzyme granulate has to be removed again in a separate step.

It was therefore the goal to develop an encapsulating system that, upon uniform application to an enzyme-containing granulate, counteracts the surface destruction of the granulate, increases the storage stability of the enzyme by encapsulation of the entire granulate, permits masking of possible intrinsic color in the unencapsulated enzyme granulate and the possible odor of the unencapsulated granulate, probably by preventing diffusion of odorous substance to the surface of the enzyme granulate.

This was attained by the invention with a granulate suitable for incorporating into especially powdered detergents or cleaning agents that contain enzymes and organic and/or inorganic carrier material, and a uniform outer, pigment-containing encapsulating layer, which is characterized by the fact that the outer encapsulating layer consists of an encapsulating system that contains 5-70 wt%, especially 10-50 wt% finely particulate inorganic water-insoluble pigment, 45-90 wt%, especially 50-85 wt% water-soluble organic material that is solid at room temperature with a melting point in the range of 40-70°C, and up to 20 wt%, preferably up to 10 wt%, and especially 1-5 wt% pourability improving agent.

The invention additionally pertains to a process for preparation of an enzyme granulate that is suitable for incorporation into powdered detergents or cleaning agents with an average particle size of 0.8-1.4 mm by extruding an enzyme premixture formed by mixing an aqueous enzyme liquid, which can be a concentrated fermentation broth, possibly freed of insoluble components by microfiltration, with an inorganic or organic carrier substance as additive, spherodization of the extrudate in

a pelletizer, possible drying, and application in a fluidized bed of extrudate of an outer encapsulating layer of a coating system containing 5-70 wt%, especially 10-50 wt% finely particulate inorganic water-insoluble pigment, 45-90 wt%, especially 50-85 wt% water-soluble organic material that is solid at room temperature with a melting point in the range of 40-70°C, and up to 20 wt%, especially 1-5 wt% pourability improving agent.

Within the frame of the present document, water-soluble materials are considered to be substances that dissolve in water to the extent of at least 50 g/L, especially at least 80 g/L, at a temperature of 30°C. According to this, fatty alcohols do not belong to the water-soluble substances.

The main component of the coating system, i.e., of water-soluble substances that are solid at room temperature, is selected from alkoxylated alcohols, fatty acids, fatty acid amides, and/or hydroxy fatty acid esters. This means preferably an alcohol, especially a primary linear alcohol with 16-22 C atoms which has been etherified with 45-120, especially 60-110 mole equivalents of alkylene oxide, especially ethylene oxide. The indicated alcohols include especially stearyl alcohol, arachidyl alcohol, behenyl alcohol, and mono to triply unsaturated alcohols of appropriate chain length, wherein it is essential that the indicated alkoxylated alcohol component have a melting point in the range of 40-70°C, especially 50-60°C, which is to be understood here as that temperature at which, upon heating, 100% of the substance is present in liquid form. Alternatively or in addition to the alcohol ethoxylates, ethoxylated fatty acids, ethoxylated fatty acid amides, and/or ethoxylation products of hydroxy fatty acid esters with 1-6 C atoms in the alcohol part of the ester, for example ricinoleic

acid, in which the degree of ethoxylation is preferably 45-120, especially 60-110, can also be used in each case. The fatty acid component of the indicated substances preferably has 12-22, especially 16-18, C atoms. The alkoxylates preferred in this connection include ethoxylation products with so-called narrow homologen distribution (NRE "narrow range ethoxylates") as they are obtained by the process of European Patent No. 339426 or International Patent Application No. 90/13533. If desired, the ethoxy groups of the indicated alkoxylation products can be replaced, at least in part, by propoxy groups. In using substance mixtures, those are also usable that contain small amounts, normally less than 15 wt%, based on the mixture, of proportions that are liquid at room temperature, as long as the overall mixture is solid at room temperature and has a solidification point in the range of 40-70°C, especially 50-60°C. The solidification point is the temperature at which solidification commences when cooling to a temperature above the melting point of the material. It can be determined with the aid of a rotating thermometer by the method of DIN/ISO 2207. Especially suited for the preparation process of the invention are substances that upon mixing with the remaining components of the encapsulating system, produce a melt that is as homogeneous as possible and can be sprayed at temperatures up to 120°C. As a guideline in this connection, it should be remembered that at the indicated temperatures, liquids with viscosities up to 500 mPa·s can be sprayed and applied onto enzyme granulates without difficulty with equipment designed for this, such as is known, for example, from German Patent Application 196 44 244.3.

Small amounts, preferably 3-10 wt%, especially 4-8 wt%, of a compound of general Formula I

$R[O(C_nH_{2n}O)_mH]_x$ (I)

in which R is an organic group with 3-12 C atoms, especially 4-10 C atoms, n is 2 or 3, m is 1-15, and x is 2 or 3, are advantageously used as additional components of the encapsulating material. Such components can be prepared in a known manner by reaction of alcohols $R(OH)_x$ with ethylene oxide and/or propylene oxide and can constitute a part of the above-indicated proportion that is liquid at room temperature. Included among the preferred compounds of general Formula I are those in which both ethoxy groups (n = 2) as well as 1,2-propoxy groups (n = 3) are contained, wherein the average number of ethoxy groups per hydroxyl group of the alcohol $R(OH)_x$ is preferably up to 10 and the average number of propoxy groups per hydroxyl group of the alcohol $R(OH)_x$ is preferably up to 5. Of these, preferably those are used in which, during preparation, the indicated alcohol was reacted first with propylene oxide and then with ethylene oxide. The preferred alcohols $R(OH)_x$ include 1,6-hexylene glycol, glycerin, and trimethylolpropane.

In a preferred embodiment of the invention, the encapsulating material system is a mixture of 10-35 wt% water-insoluble inorganic pigment, 10-40 wt%, especially 15-30 wt% of the above-indicated ethoxylated fatty acid, 15-77 wt%, especially 27-71 wt%, of the above-indicated ethoxylated fatty alcohol, and 3-10 wt%, especially 4-8 wt% of the compound of general Formula I.

Water-insoluble inorganic pigments with which possibly offensive coloration of the enzyme granulate can be masked can include, for example, calcium carbonate, titanium dioxide (which

can be present in the rutile or anatase crystalline form), zinc oxide, zinc sulfide, white lead (basic lead carbonate), barium sulfate, aluminum hydroxide, antimony oxide, lithopone (zinc sulfide-barium sulfate), kaolin, chalk, talc, and/or mica. These are present in such a finely particulate form that they can be dispersed into a melt of the remaining components of the coating system. Usually, the average particle size of such pigments is in the range of 0.004-50 μm. The use of pigments that are surface-modified with dispersants is also possible. Preferably titanium dioxide pigments, especially in the rutile form, that have been surface-modified with Al, Si, Zr or polyol compounds can be used as they are marketed, for example, under the trade name Kronos® 2132 (Kronos-Titan Co.) or Hombitan® R 522 (Sachtleben Chemie GmbH). Also usable are the Tiona® RLL, AG, or VC types from Solvay Co. as well as Bayertitan® RD, R-KB, and AZ types from Bayer AG.

As additional components of the encapsulating system, pourability improvers can be considered. These are considered to be active substances whose absence leads to worsening of the pourability of the encapsulated granulate. Useful are, for example, aluminum silicates, zeolites, sodium silicates, or silica which are mixed in finely particulate form with the other components of the encapsulating system for application to the enzyme granulate; or they can be applied separately after application of the other components of the encapsulating system.

As enzymes, primarily proteases, lipases, amylases, and/or cellulases recovered from microorganisms such as bacteria or fungi can be considered, wherein proteases produced by *Bacillus* species as well as mixtures thereof with amylases are preferred. They are recovered in a known manner from suitable microorganisms

by fermentation processes that are described, for example in German Patent Nos. 19 40 488, 20 44 161, 22 01 803, and 21 21 397, US Patent Nos. 3 632 957 and 4 264 738, as well as European Patent Application No. 006 638. The process of the invention can be especially advantageously used for preparing assembly ready-to-use, very active proteases as they are known, for example, from International Patent Application No. 91/2792 because of their storage stable incorporation into detergents and cleaning agents often presents problems and, according to the invention, the formation of undesired enzyme dust is avoided. The enzymes are contained in the granulates of the invention preferably in amounts of 4-20 wt%. In case the enzyme granulate of the invention is a protease-containing formulation, the protease activity is preferably 150000 protease units (PU, determined by the method described in Tenside 7 (1970), p. 125) to 350000 PU, especially 160000 PU to 300000 PU per gram of enzyme granulate.

As carrier material for the enzyme, in principle all organic or inorganic powdered substances can be used that do not destroy or deactivate, or do so only to a tolerable extent, the enzymes, and which are stable under granulation conditions. Such substances include, for example, starch, cereal flour, cellulose powder, alkali aluminosilicate especially zeolites, layered silicates for example bentonite or smectite, and water-soluble inorganic salts for example alkali chloride, alkali sulfate, alkali carbonate, or alkali acetate, wherein sodium or potassium are the preferred alkali metals. Preferably a carrier material mixture is used that contains water in a swellable starch as well as possibly cereal flour, cellulose powder, and/or alkali carbonate.

The water-swellable starch is preferably corn starch, rice starch, potato starch or mixtures thereof, wherein the use of corn starch is especially preferred. Swellable starch is preferably contained in the enzyme granulates of the invention in amounts of 20-50 wt%, especially 25-45 wt%.

The cereal flour that is possibly included is especially a product that can be produced from wheat, rye, barley, or oats or is a mixture of these flours wherein whole grain flour is preferred. In this, whole grain four is understood to be incompletely milled flour that was prepared from whole, unhulled kernels and at least primarily consists of such a product wherein the rest consists of fully milled flour or starch. Preferably commercial wheat flour qualities such as Type 450 or Type 550 are used. Cereal types leading to flour products of the above-indicated swellable starches can also be used if attention is paid to the fact that the flour is prepared from whole kernels. As is well known, the flour component of the additive mixture produces a substantial reduction in the odor of the enzyme preparation which is far superior to odor reduction by incorporation of equal amounts of appropriate types of starch. Such cereal flour is preferably contained in the enzyme granulates of the invention in amounts up to 35 wt%, especially 15-25 wt%.

As additional components of the carrier material, the enzyme granulates of the invention contain preferably 1-50 wt%, especially 5-25 wt%, based on the total granulate, of a granulating aid system that contains alkali carboxymethylcellulose with degrees of substitution of 0.5-1 and polyethylene glycol and/or alkylpolyethoxylate. This granulating aid system preferably contains 0.5-5 wt%, in each case based on

the finished enzyme granulate, alkali carboxymethylcellulose with degrees of substitution of 0.5-1 and up to 3 wt% polyethylene glycol and/or alkylpolyethoxylate, wherein it is especially preferred that it contain at least 0.5 wt%, especially 0.8-2 wt% polyethylene glycol with an average molecular mass below 1000 and/or alkylpolyethoxylate with at least 30 ethoxy groups in case more than 2 wt% alkali carboxymethylcellulose is contained therein. More highly substituted carboxymethylcellulose with degrees of substitution up to 3 is preferably not contained in the granulating aid system.

Phosphated, possibly partially hydrolyzed starches can also be considered as granulating aids. Phosphated starches are understood to be starch derivatives in which the hydroxyl groups of the anhydroglucose units of the starch have been replaced by the $-O-P-(O)(OH)_2$ group or its water-soluble salts, especially alkali salts such a sodium and/or potassium salts. The average degree of phosphating of the starch is understood to be the number of esterified, phosphate group carrying oxygen atoms per saccharide monomer of the starch averaged over all the saccharide units. The average degree of phosphating of the phosphated starches that are preferably used is in the range of 1.5-2.5 since in using these, much lesser amounts are required to attain a certain granulate strength than when using carboxymethylcellulose. Partially hydrolyzed starches are understood within the frame of the present invention to be oligomers or polymers of carbohydrates that can be obtained by partial hydrolysis of starch by conventional acid- or enzyme catalyzed processes. Preferably hydrolysis products are involved with an average molecular mass in the range of 440-500,000. Preferred are polysaccharides with a dextrose equivalent (DE) in

the range of 0.5-40, especially 2-30, wherein DE is a conventional measure for the reducing effect of a polysaccharide compared to dextrose which has a DE of 100. Usable after phosphating are both maltodextrins (DE 3-20) and dried glucose syrup (DE 20-37) as well as so-called yellow dextrins and white dextrins with a higher average molecular mass in the range of 2000-30000. Based on the finished granulate, a content of 0.1-20 wt%, especially 0.5-15 wt% phosphated starch is preferred.

As additional components of the granulating aid system, possibly additional cellulose or starch ethers can be contained such as carboxymethylstarch, methylcellulose, hydroxyethylcellulose, hydroxypropylcellulose, as well as appropriate mixed ethers of cellulose, gelatin, casein, tragacanth, maltodextrose, saccharose, invert sugar, glucose syrup, or other oligomers or polymers of natural or synthetic origin that are easily soluble or dispersible in water. Usable synthetic water-soluble polymers are polyacrylates, polymethacrylates, copolymers of acrylic acid with maleic acid or vinyl group containing compounds; additionally, polyvinyl alcohol, partially saponified polyvinyl acetate, and polyvinylpyrrolidone. Insofar as the above-indicated compounds are ones with free carboxyl groups, they are normally present in the form of their alkali salts, especially their sodium salts. Such additional granulating aids can be contained in the enzyme granulates of the invention in amounts up to 10 wt%, especially 0.5-8 wt%. Although higher molecular weight polyethylene glycols, that is, those with an average molecular weight more than 1000, are usable as synthetic water-soluble polymers with a dust-binding effect, but specifically the higher molecular weight polyethylene glycols produce an undesired increase in the

dissolution time that is needed for the granulate, so that these substances are preferably completely absent in the enzyme granulates of the invention.

For preparation of the enzyme granulates of the invention, one advantageously proceeds from the fermentation broth, which can be freed of insoluble accompanying substances, for example by microfiltration. In this, the microfiltration is preferably done as counterflow microfiltration using porous tubes with micropores larger than 0.1 mm, concentrate solution flow rates greater than 2 m/s, and a pressure difference to the permeate side of less than 5 bar, for example as described in European Patent Application No. 200 032. Subsequently, the microfiltration permeate is concentrated, preferably by ultrafiltration, possibly with subsequent vacuum evaporation. In this, the concentrating can be done as described in International Patent Application No. 92/11347 in such a manner that one only obtains a relatively low content of solids of preferably 5-50 wt%, especially 10-40 wt%. The concentrate is added to a dry, powdered to particulate mixture of the above-described additives that has suitably been pre-formulated. The water content of the mixture should be chosen in such a manner that upon processing with stirring and impacting equipment, it is converted to grains of particles that do not stick at room temperature and in using higher pressures can be plastically deformed and extruded. The pourable premixture in principle is processed in a kneader in a known manner and in a connected extruder to produce a plastic mass that is as homogeneous as possible, wherein as a consequence of mechanical working of the mass, it can heat up to temperatures between 40°C-60°C, especially 45-55°C. The products that leave the extruder pass through a perforated disk with a following

strike-off knife and are thereby commind to cylinder-shaped particles of a specific size. The diameter of the holes in the perforated disk are suitably 0.7-1.2 mm, preferably 0.8-1.0 mm. The particles in this form can subsequently be dried and coated with the encapsulating system of the invention. However, it has been shown to be more advantageous to spherodize the cylindrical particles leaving the extruder and chopper prior to encapsulating them; this means to round them off and to remove burrs in suitable equipment. For this, an arrangement is used that consists of a cylindrical vessel with stationary fixed side walls and a rotating friction plate on the bottom. Equipment of this kind is marketed in the field under the trade name Marumerizer® and is described, for example, in German Patent Nos. 21 37 042 and 21 37 043. Subsequently, possibly occurring dusty parts with a particle size of less than 0.1 mm, especially less than 0.4 mm, as well as possible coarse parts with a particle size greater than 2 mm, especially greater than 1.6 mm, can be removed by screening or air separation and can possibly be recycled to the production process. After spherodization, the small spheres are dried continuously or batch-wise using fluidized bed drying equipment at inlet temperatures of preferably 35-50°C, and especially at a product temperature of not more than 42°C to produce a desired a residual moisture content of, for example, 4-10 wt%, especially 5-8 wt%, based on the entire granulate, if they previously had a higher water content.

Instead of, after, or preferably during drying, the encapsulating system of the invention is applied as an outer coating. In a preferred embodiment of the preparation process of the invention, the encapsulation system is applied to the extrudate, with possible cooling, as a heated organic

water-soluble component that is solid at room temperature and which is present as a liquid at a temperature of 5-45°C above the melting point. Preferably, 5-25 wt% of the encapsulating system, based on the finished granulate, is applied as outer coating to the enzyme-containing extrudate.

The enzyme preparation obtained by the process of the invention consists primarily of rounded, uniformly coated, and dust-free particles that generally have a bulk density of 500-900 g/L, especially 650-880 g/L. The 100% granulates of the invention are characterized by very high storage stability, especially at temperatures above room temperature and at high relative humidities as well as by rapid and complete dissolution in the wash bath. The granulates of the invention preferably liberate their enzyme activity in water at 25°C within 3 min, especially within 90 sec to 2 min.

The process of the invention or enzyme granulates prepared by the process of the invention are advantageously used for preparation of particulate, especially powdered detergents or cleaning agents which can be obtained by simple mixing of the enzyme granulates with additional powder components that are usual in such agents. For incorporation into powdered detergents and cleaning agents, the enzyme granulate preferably has an average particle size in the range of 0.8-1.2 mm. The granulates of the invention preferably contain less than 2 wt%, especially at most 1.4 wt%, particles with particle sizes outside the range of 0.4-1.6 mm.

Examples

Example 1

A harvested slurry recovered from fermentation as described in International Patent Application No. 91/2792 with 75000 protease units per g (PU/g), was concentrated after removal of fermentation residues by decanting and microfiltration in ultrafiltration equipment. After additional concentrating by means of vacuum evaporation, the aqueous enzyme suspension contained 700000 PU/g. This protease concentrate was mixed with additives (6 wt% saccharose, 4 wt% cellulose, 5 wt% carboxymethylcellulose with a degree of substitution of 0.65-0.75, 16 wt% wheat flour, 36 wt% corn starch, and 3 wt% polyethylene glycol with an average molecular weight of 2000 (the amounts are based on the resulting mixture in each case), was homogenized, and subsequently converted to granulates in an extruder with a cutting device. The diameter of the holes in the perforated plate in the extruder was 0.85 mm. The length-to-thickness ratio of the granulate particle was 1. After rounding and drying of the granulate, particles with particle size less than 0.4 mm and larger than 1.6 mm were screened out. The particle fraction between 0.4 mm and 1.6 mm was coated with a coating in a type GPCG-5 rotor granulator from Glatt Co., wherein a coating melt of 70 wt% 80-fold ethoxylated $C_{16/18}$ fatty alcohol (Lutensol® manufacturer BASF) and 30 wt% titanium dioxide were used. 16 wt% (based on the enzyme granulate formed) of the melt obtained at 120°C was sprayed onto the enzyme granulate under the following operating conditions:

Amount of enzyme granulate used: 10 kg
Inlet air temperature: 40°C

Product temperature: 42°C
Outlet air temperature: 41°C
Amount of air: 150 m^3/h
Rotor: 260 rpm
Dual nozzle spraying air temperature: 120°C
Dosing rate of the coating melt: 50 g/min.

The coating material formed a uniform non-porous film on the granulate surface. To determine the dust abrasion, 60 g of the thus-prepared granulate P1 was placed in a fluidized bed. The waste air from the fluidized bed flowed through a filter. The amount of dust trapped after 40 min residence time of the enzyme granulate under these conditions corresponds to the amount of dust abrasion. In the present case, the dust abrasion at less than 10 mg per filter was negligibly small.

Example 2

Example 1 was repeated but wherein only one coating melt consisting of 20 wt% titanium dioxide, 48 wt% 80-fold ethoxylated $C_{16/18}$ fatty alcohol, 25 wt% 80-fold ethoxylated $C_{16/18}$ fatty acid, and 7 wt% trimethylolpropane that had been reacted with 3 equivalents of propylene oxide and 7 equivalents ethylene oxide per hydroxyl group were used. Here too, a granulate (P2) was obtained with negligibly small dust abrasion.

Example 3

To determine the residue-free dissolution of the enzyme granulate, 1000 mL water (16°dH tempered at 30°C) was placed in a

2000 mL beaker (tall form); a laboratory stirrer with a propeller stirring head was fixed in a central position 1.5 cm from the bottom of the beaker and set into motion at 800 rpm. 8 g of the granulate to be tested were strewn in and stirred for 90 sec. Subsequently, the liquid in the beaker was poured through a screen (mesh width 0.2 mm) of known weight; the beaker was rinsed with as little cold water as possible and after drying at 40°C to constant weight, the screen was weighed. The screening residues (dual determinations) shown in Table II wherein, besides granulates P1 and P2 of the invention, an enzyme granulate V1 of the state of the art was tested for comparison which had the same amount of coating material but which consisted of 78 wt% C_{18} fatty alcohol, 4% 40-fold ethoxylated $C_{16/18}$ fatty alcohol, and 18 wt% titanium dioxide.

Table II. Enzyme granulate screening residues

Enzyme granulate	Screening residue (wt%)
P1	2.5
P2	2.5
V1	96.0

Claims

1. Enzyme granulate suitable for incorporation into especially powdered detergents or cleaning agents containing enzyme and inorganic and/or organic carrier material and a uniform outer, pigment-containing encapsulating layer, characterized by the fact that the outer encapsulating layer consists of an encapsulating system that contains 5-70 wt% finely

particulate inorganic water-insoluble pigment, 45-90 wt% water-soluble organic material that is solid at room temperature with a melting point in the range of 40-70°C, and up to 20 wt% pourability improving agent.

2. Enzyme granulate as per Claim 1, characterized by the fact that the encapsulating system contains 50-85 wt% water-soluble organic material that is solid at room temperature.

3. Enzyme granulate as per Claim 1 or 2, characterized by the fact that the encapsulating system contains 10-50 wt% finely particulate inorganic water-insoluble pigment.

4. Enzyme granulate as per one of Claims 1-3, characterized by the fact that the encapsulating system contains up to 10 wt%, preferably 1-5 wt%, pourability improving agent.

5. Enzyme granulate as per one of Claims 1-4, characterized by the fact that water-soluble substance that is solid at room temperature is a primary, linear, saturated or unsaturated alcohol with 16-22 C atoms that has been etherified with on average 45-120, especially 60-110, mole equivalents of ethylene oxide, an ethoxylated fatty acid, an ethoxylated fatty acid amide, an ethoxylation product of hydroxy-fatty acid esters with 1-6 C atoms in the alcohol part of the ester, wherein the degree of ethoxylation in each case is especially 45-120, or a mixture thereof.

6. Enzyme granulate as per one of Claims 1-5, characterized by the fact that it contains as additional component of the encapsulating material, small amounts of a compound of general Formula I

$$R[O(C_nH_{2n}O)_mH]_x \qquad (I)$$

in which R is an organic group with 3-12 C atoms, especially 4-10 C atoms, n is 2 or 3, m is 1 to 15, and x is 2 or 3.

7. Enzyme granulate as per Claim 6, characterized by the fact that the compounds of Formula I are prepared by reaction of alcohols $R(OH)_x$ with ethylene oxide and/or propylene oxide and contain both ethoxy groups (n = 2) as well as 1,2-propoxy groups (n = 3), wherein the average number of ethoxy groups per hydroxyl group of the alcohol $R(OH)_x$ is preferably up to 10 and the average number of propoxy groups per hydroxyl group of the alcohol $R(OH)_x$ is preferably up to 5.

8. Enzyme granulate as per one of Claims 1-7, characterized by the fact that the encapsulating system is a mixture of 10-35 wt% water-insoluble inorganic pigment, 10-40 wt%, especially 15-30 wt% ethoxylated fatty acid, 15-77 wt%, especially 27-71 wt% ethoxylated fatty alcohol, and 3-10 wt%, especially 4-8 wt% of the compound of general Formula I.

9. Enzyme granulate as per one of Claims 1-8, characterized by the fact the encapsulating layer contains calcium carbonate, titanium dioxide, zinc oxide, zinc sulfide, white lead, barium carbonate, barium sulfate, aluminum hydroxide, antimony oxide, kaolin, chalk, talc, and/or mica as inorganic pigment.

10. Enzyme granulate as per one of Claims 1-9, characterized by the fact it contains protease, amylase, lipase, and/or cellulase.

11. Enzyme granulate as per one of Claims 1-10, characterized by the fact it contains protease with an activity of 150000 PU to 350000 PU, especially 160000 PU to 300000 PU per gram of enzyme granulate.

12. Process for preparation of an enzyme granulate suitable for incorporation into powdered detergents or cleaning agents

with an average particle size of 0.8-1.4 mm by extrusion of a pre-mixture obtained by mixing of an aqueous enzyme liquid with inorganic and/or organic carrier materials as additives, spherodization of the extrudate in a rounding apparatus, and application of an outer encapsulating layer, wherein an outer encapsulation layer of an encapsulating system that contains 5-70 wt%, especially 10-50 wt% finely particulate inorganic water-insoluble pigment, 45-90 wt%, especially 50-85 wt% water-soluble organic material that is solid at room temperature with a melting point in the range of 40-70°C, and up to 20 wt%, especially 1-5 wt% pourability improving agent, is applied in a fluidized bed of extrudate.

13. Process as per Claim 12, characterized by the fact that the aqueous enzyme liquid is a concentrated fermentation broth possibly freed of insoluble components by microfiltration.

14. Process as per Claim 12 or 13, characterized by the fact that 5-25 wt% of the coating system, based on the finished granulate, is applied to the enzyme-containing extrudate as outer encapsulating layer.

15. Process as per one of Claims 12-14, characterized by the fact that the coating system is applied to the extrudate as a liquid of water-soluble organic material that is solid at room temperature at a temperature of 5-45°C above the melting point.

16. Process as per one of Claims 12-15, characterized by the fact that the encapsulating system is a mixture of 10-35 wt% water-insoluble inorganic pigment, 10-40 wt%, especially 15-30 wt% ethoxylated fatty acid, 15-77 wt%, especially 27-71 wt% ethoxylated fatty alcohol, and 3-10 wt%, especially 4-8 wt% of the compound of general Formula I.

17. Use of an enzyme granulate as per one of Claims 1-11 or which can be obtained by the process of Claims 12-16 for preparation of solid, especially powdered, detergents or cleaning agents.